

The Effect of Porosity and Curing Conditions on the Bands of the Infrared Spectroscopy in Blend Cement Pastes

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FT-IR spectroscopy is employed to investigate the effect of the local porosity, i.e., water to cement (w/c) ratio, at two different curing times of 3 and 28 days on the bands spectra in the ordinary Portland cement pastes (OPC) in the spectral range 400 to 4000 cm⁻¹. The study revealed the characteristic changes in the stretching and bending vibration modes of the SiO₄ group (≈ 460 cm⁻¹), the stretching vibration modes of the C-O and of C=O bonds (≈ 970 cm⁻¹, and 1430 cm⁻¹) (the strong absorption of the CO₃²⁻ group in the lattice region), and finally, the stretching vibration of the water molecules (vibration of the OH group of the Portland CH phase). The results have indicated that the critical conditions for the change accompanying these vibration modes during the hydration mechanism of the OPC samples occur at (w/c) ratio of 0.3, and 0.35 independently of the hydration time.

1. Introduction

Our knowledge and understanding of the vibration mechanism of the fundamental vibration modes in the OPC matrix system have been increased marginally upon the determination of the molecular structure, identification of the chemical for cement pastes and its rate of hydration products during the hydration mechanism of the matrix cement system. Also, the FT-IR analysis has been used to resolve the changes in the frequency of the assignment bonds and to monitor the dynamic changes in the vibration motion of the principal modes group of the matrix cement system during the hydration reaction mechanism to produce the

principal phases (CSH and CH) and other phases as hydration products from the hydration mechanism [1,2].

The investigation of the hydration mechanism in the blended cement pastes by FT-IR analysis method has been found to be very useful in identifying most of the rate hydration mechanism (phase transformation & microstructural) of the hydrated products, through the variation in the bonds for the fundamental vibration modes, which are present in the cement matrix system. The alternation of the bonding characteristics in the principal vibration modes in the hydrated cement matrix system can be described by the correlation between the changes in the physical properties and the hydration behavior of the cement matrix system under different hydration conditions [3,4].

The analysis of the FT-IR spectroscopy of the cement mortars matrix system through the variation of the fundamental vibration absorption bands in the region $400 - 4000 \text{ cm}^{-1}$ (stretching, bending and vibration modes), have been varied, depending on some parameters such as the curing conditions for the hydration mechanism, molecular structure, chemical bonds, crystal form of the hydration products phases and the impurities present in the cement matrix system [5,6].

This paper presents the results obtained from the FT-IR spectroscopy on studying and analyzing the changes accompanying in the fundamental vibration modes in the OPC matrix system. The analysis includes the variation of band shape, relative integrated intensity (R.I.), absorbance (A), relaxation time (t), and the rotational energy barrier (U) under the effect of the changes in the local porosity (w/c ratio) and at different curing times of hydration (3 and 28 days).

2. Experimental

Samples used in this investigation were prepared from OPC with different porosity, i.e., different (w/c) ratio (0.25, 0.30, 0.35, and 0.40) at room temperature and different curing times of 3, and 28 days [7]. The chemical composition of the used OPC is illustrated in Table(1).

The infrared measurements were carried out using the FT-IR type Perkin Elmer 1600 spectrometer. The prepared samples consisted of 2.5 mg of the powder samples, mixed with 1.0 mg powder KBr and then placed in a cylindrical die of 10.0 mm diameter after shaking the mixture

for about half a minute. The die was evacuated insuring dryness and then the sample was pressed. A clear disc of approximately 1.0mm thickness was obtained. The infrared spectrum was recorded in the region 400 to 4000 cm^{-1} by the computerized system.

Table (1) : Chemical Analysis of The Used OPC Samples

	<i>SiO₂</i>	<i>TiO₂</i>	<i>Al₂O₃</i>	<i>Fe₂O</i>	<i>FeO</i>	<i>MgO</i>	<i>CaO</i>	<i>Na₂O</i>	<i>K₂O</i>	<i>P₂O₅</i>	<i>H₂O</i>	<i>SO₃</i>	<i>Cl</i>
OPC	20.85	0.28	4.7	3.86	0.16	1.6	61.71	0.967	0.25	0.61	0.68	2.9	-

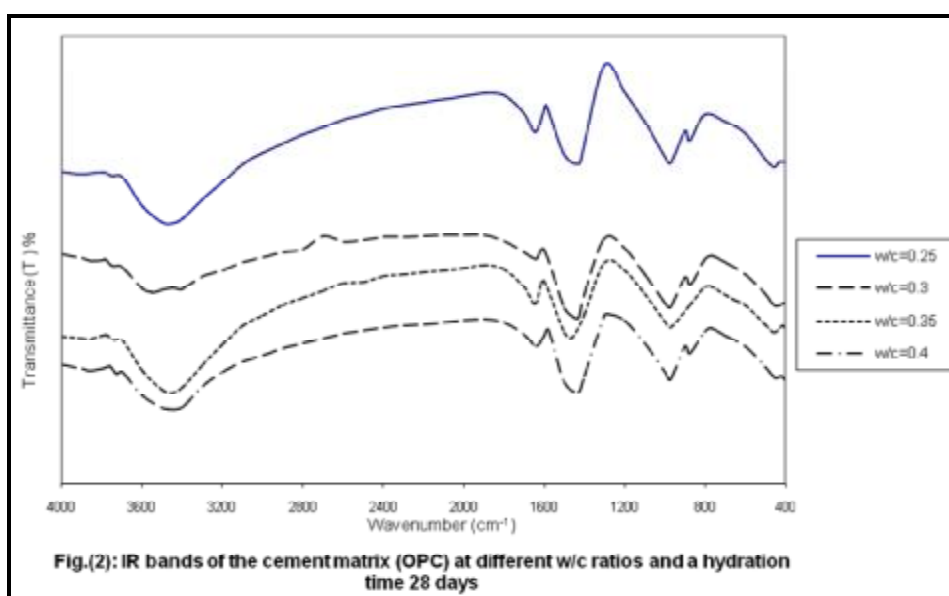
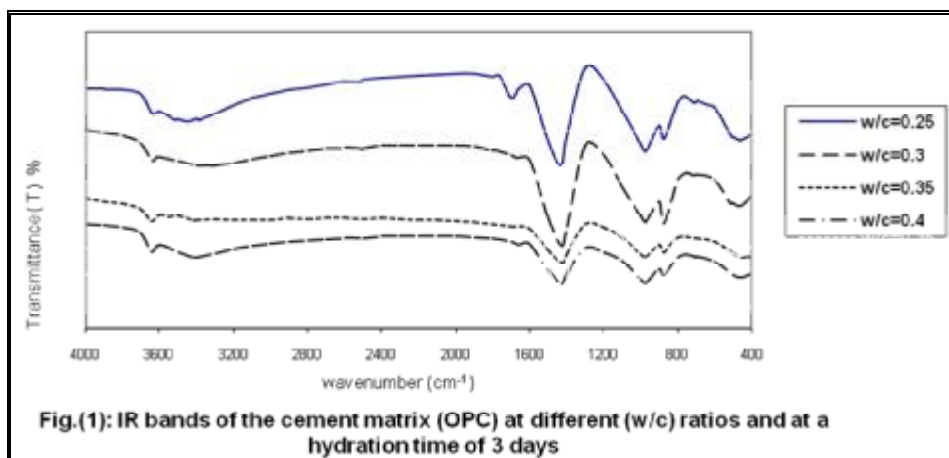
3. Results and Discussion

The FT-IR analysis of prepared samples was taken at different values of the (w/c) ratio (0.25, 0.30, 0.35, and 0.40). In the following IR results, we use the analysis of the IR spectrum for cement materials samples as an important useful method in order to recognize the molecular and frequency bands, and to know the involved mechanism and reasons for decreasing or increasing the rate of hydration process inside the cement matrix. So we have identified the frequency bands for cement matrix, which are denoted in Table (2).

Table (2) : IR Spectral Data of Hydrated OPC

modes	Frequency assignment (cm^{-1})	Types of the mode assignment
n_1	460	Bending vibration mode of SiO_4 group
n_2	970	Stretching vibration of carbon-oxygen double bands
n_3	1430	Strong absorption of CO_3^{2-} group in the lattice region
n_4	3550	Stretching vibration of the OH bonds

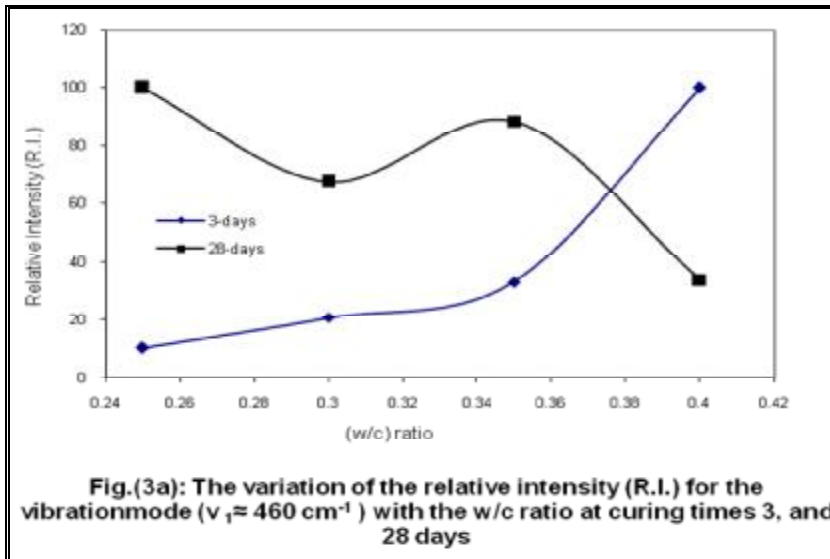
The FT-IR analysis of the hydrated OPC samples are shown in Fig.(1) and Fig.(2) at hydration times of 3 and 28 days respectively and different (w/c) ratio (i.e. different porosity). In the following IR results, we will clarify the internal fundamental normal vibrations of the OPC matrix samples in the frequency bands ($n_1 \approx 460$, $n_2 \approx 970$, $n_3 \approx 1430$, and $n_4 \approx 3550 \text{ cm}^{-1}$).

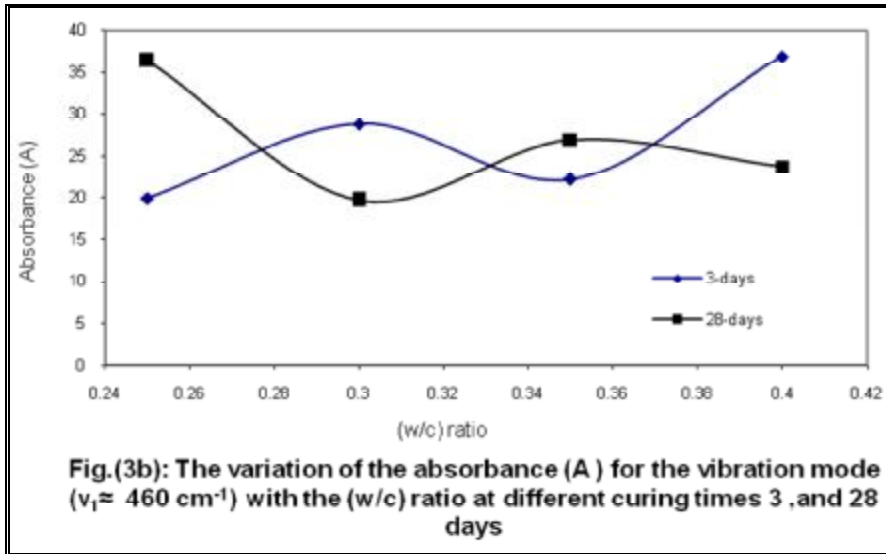


The changes in these frequency bands (n_1 , n_2 , n_3 , and n_4) for the matrix samples at different porosity and a hydration time of 3 days is shown in Fig.(1). From this figure, we can easily notice the changes in the capillary porous system. Here, increasing the (w/c) ratio of the sample will lead to an increase in the degree of hydration reaction (high stability). That is mainly dependent on the group of the vibration modes in the samples under consideration, as compared with the samples made with a lower (w/c) ratio [8]. For prolonged hydration lasting for 28 days, the changes in the internal modes of vibration for the different matrix

cement samples are clearly observed in Fig.(2). From this figure, completely different modes are seen as compared to those observed at the curing time of 3 days. That could be related to the formation of substantial hydration products that precipitated in the pores samples of the OPC, which are originally filled with water, together with the increase in the hydraulic properties of these cement samples [9].

The variation of the relative peak intensity (R.I.), and the absorbance (A) for the vibration mode ($\nu_1 \approx 460 \text{ cm}^{-1}$) are shown in Figs.(3a,b). The absorbance (A) of the vibration mode ($\nu_1 \approx 460 \text{ cm}^{-1}$) is determined from the relation $A = \log(1/T)$, where "T" is the transmittance of the mode [10]. The variation in both (R.I.) and (A) in this mode are clearly depending on the rate of changes in the capillary pores in the different samples. The critical variations in the (R.I.) and (A) occurs at ($w/c = 0.3$ & 0.35) whatever the curing hydration time being 3 or 28 days. Also this bending mode is decreasing with increasing the curing time and the (w/c) ratio being indicative of the increase of the hydration mechanism processes with the curing time and the capillary pores of the matrix cement system. This mode of vibration for the SiO_4 groups are responsible for the formation and transformation of the microstructure and the gel like structure of the C-S-H hydrated phase during the hydration mechanism of tricalcium silicate hydrate (Ca_3Si) leading to the transformation equilibrium that would be allowed and enhanced [11].





The changes in the relative peak intensity (R.I.), absorbance (A), relaxation time (t), and the rotational energy barrier (U) for the vibration mode ($n_2 \approx 970 \text{ cm}^{-1}$) with the (w/c) ratio at curing times of 3 and 28 days are shown in Figs.(4a-d). The rotational energy barrier (U) and the relaxation time (t) are determined by using the following relaxation time equation [12], at the room temperature ($\approx 25 \text{ }^\circ\text{C}$).

$$t = t_0 \exp\left(\frac{U}{kT}\right) \quad (1)$$

where “U” is the rotational barrier energy, “k” is Boltzman’s constant, and “T” is the absolute temperature, and $t_0 = 10^{-11}$ sec . Initially, the relaxation time “t ” is determined by applying the following relation [13],

$$t = \frac{1}{p \cdot \Delta n \cdot c} \quad (2)$$

where Δn is the half band width of the absorption band and “c” is the light velocity. From Figs.(4a-d), it can be easily shown that the changes in the relative peak intensity (R.I.), absorbance (A), rotational barrier energy (U), and the relaxation time (t) are mainly dependent on the rate of porosity (i.e., w/c ratio) inside the matrix samples at curing times of 3 and 28 days. The critical variation in all optical parameters occurs at w/c ≈ 0.3 and 0.35 as in the case of the vibration band mode ($n_1 \approx 460 \text{ cm}^{-1}$).

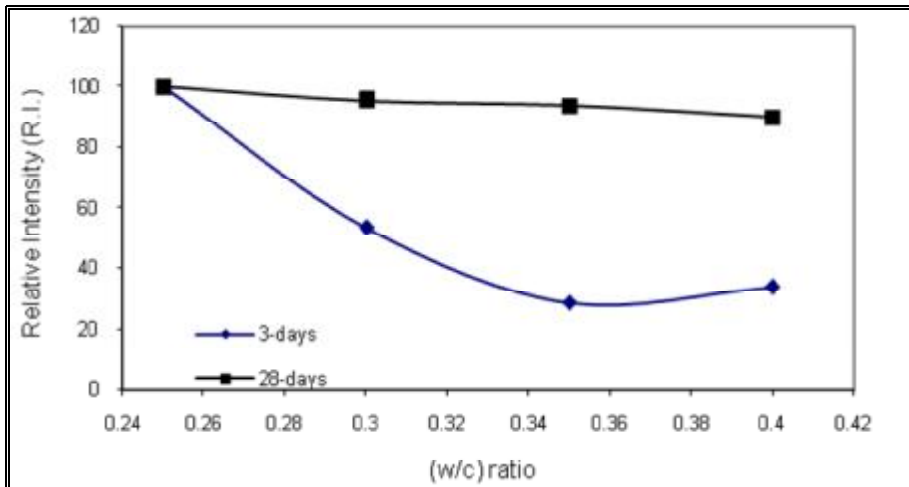


Fig.(4a): The changes in the relative intensity (R.I.), for the vibration mode ($\nu_2 \approx 970 \text{ cm}^{-1}$) with the w/c ratios at different curing times 3, and 28 days

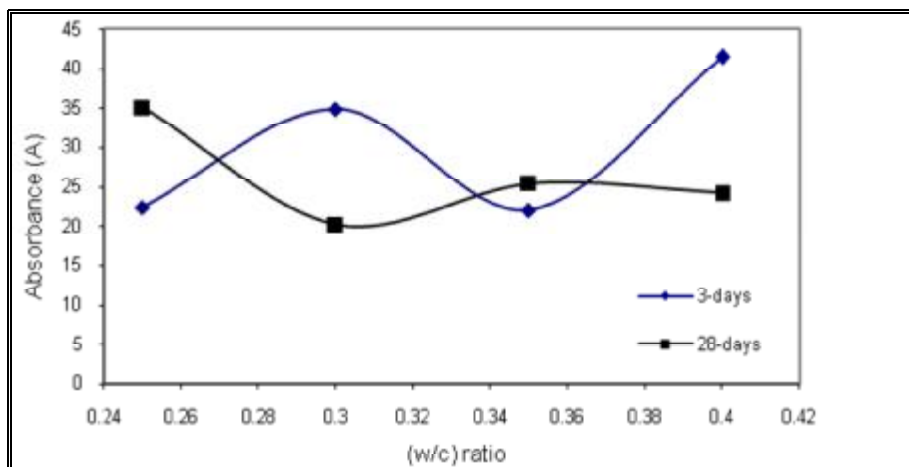
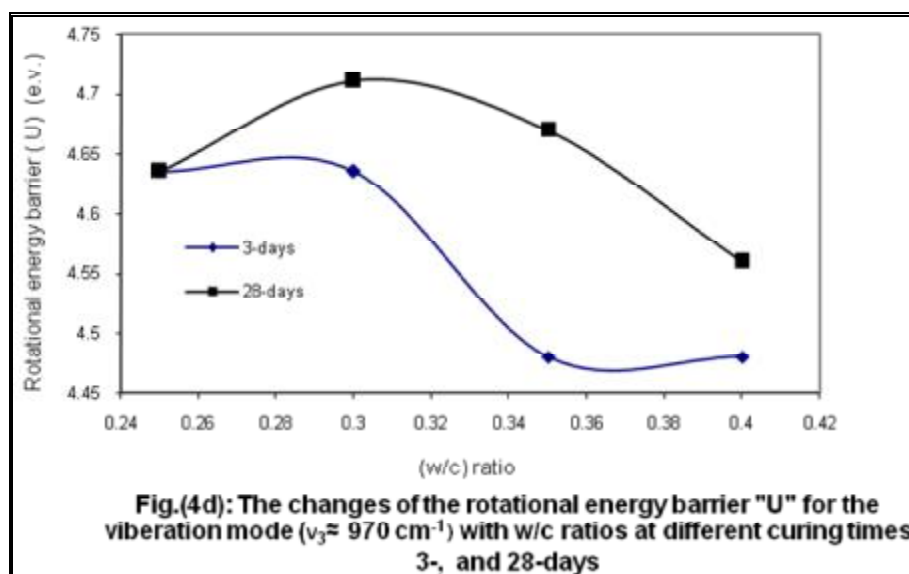
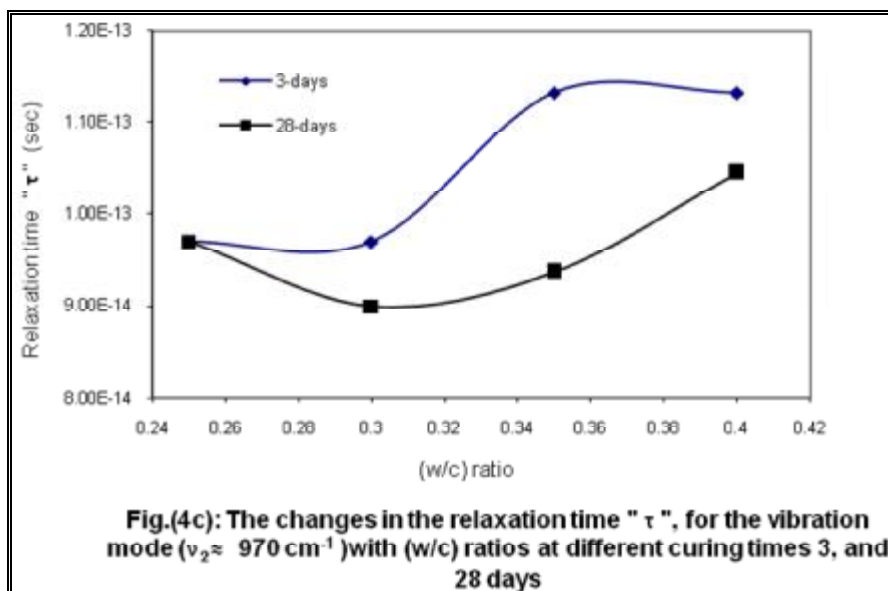
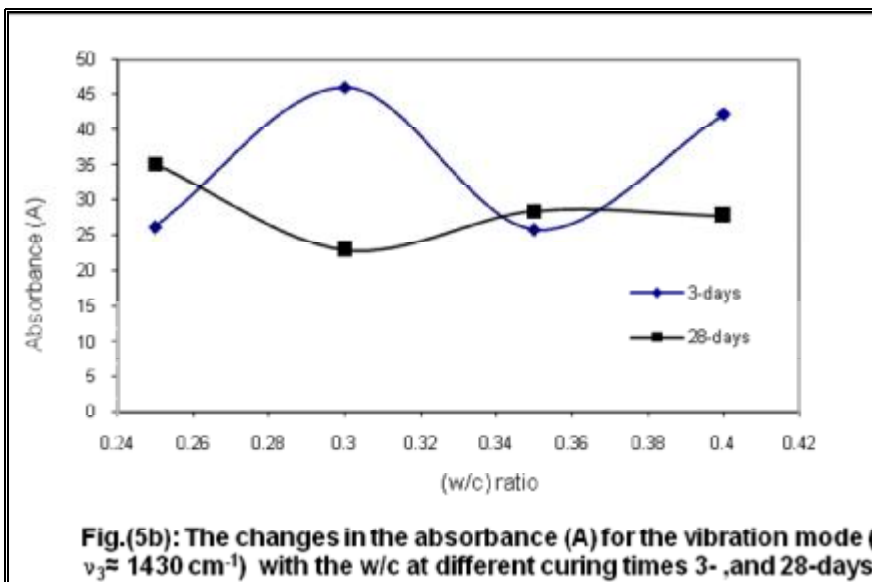
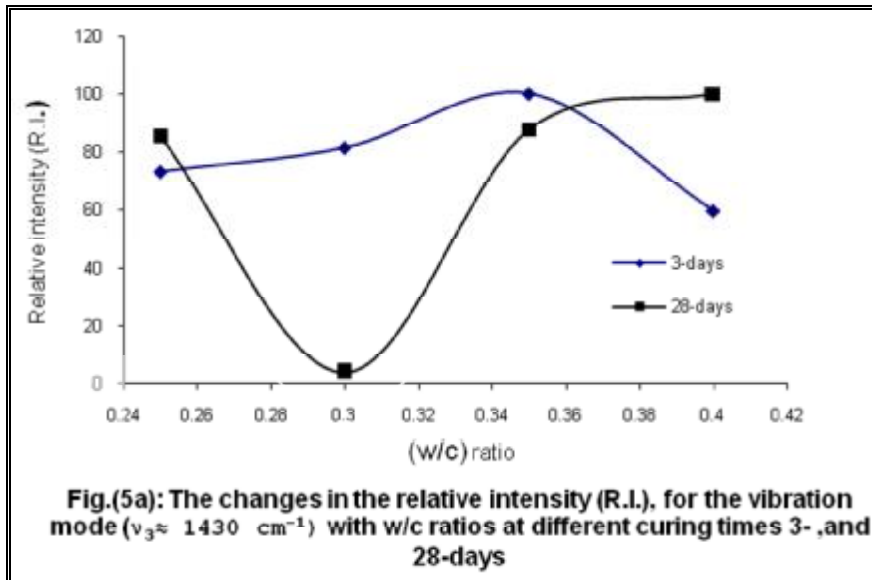


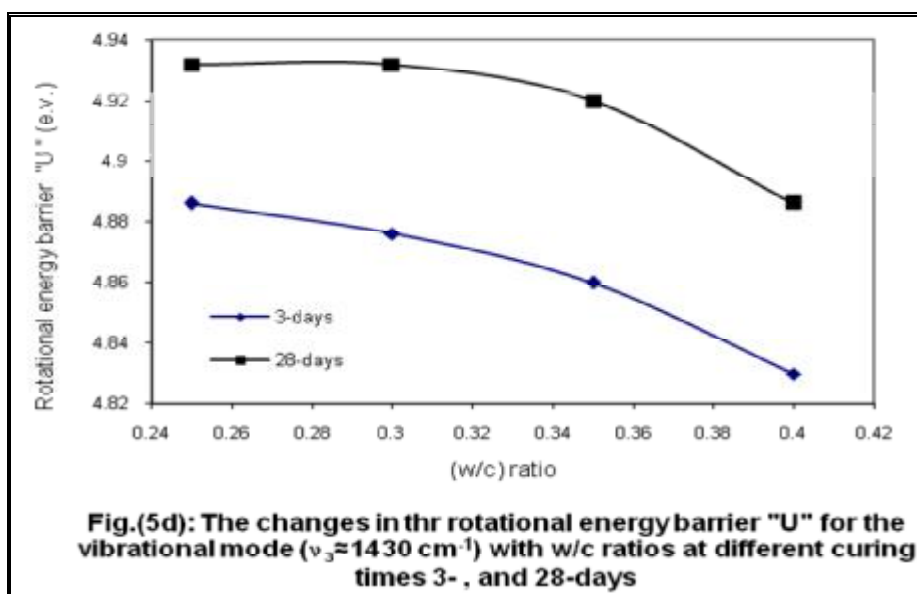
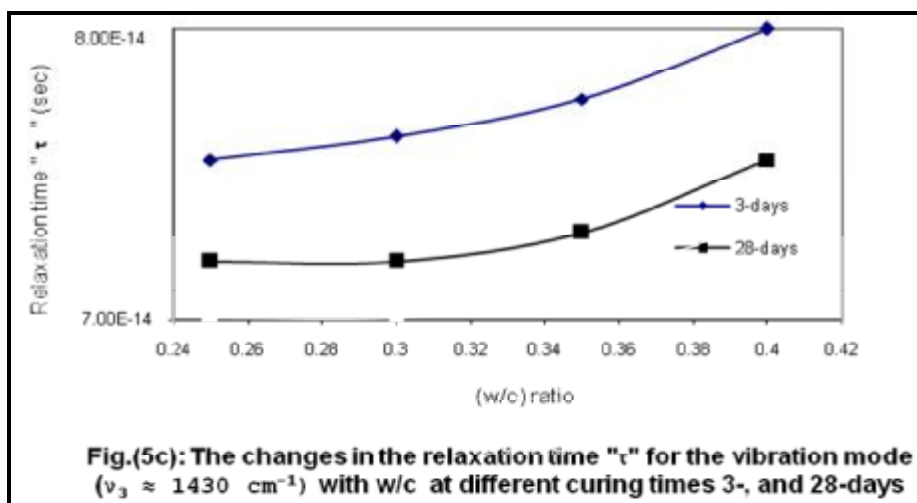
Fig.(4b): The changes in the absorbance (A), for the vibration mode ($\nu_2 \approx 970 \text{ cm}^{-1}$) with (w/c) ratios at different curing times 3 and 28 days



The band mode ($\nu_2 \approx 970 \text{ cm}^{-1}$), is related to the single bond of C-O, which is formed through the chemical reaction of CaCO_3 with H_2O during the hydration mechanism. This mode is clearly depending on the rate of changes of the local porosity of the matrix cement samples and the curing conditions inside the matrix for all different cement samples [14].

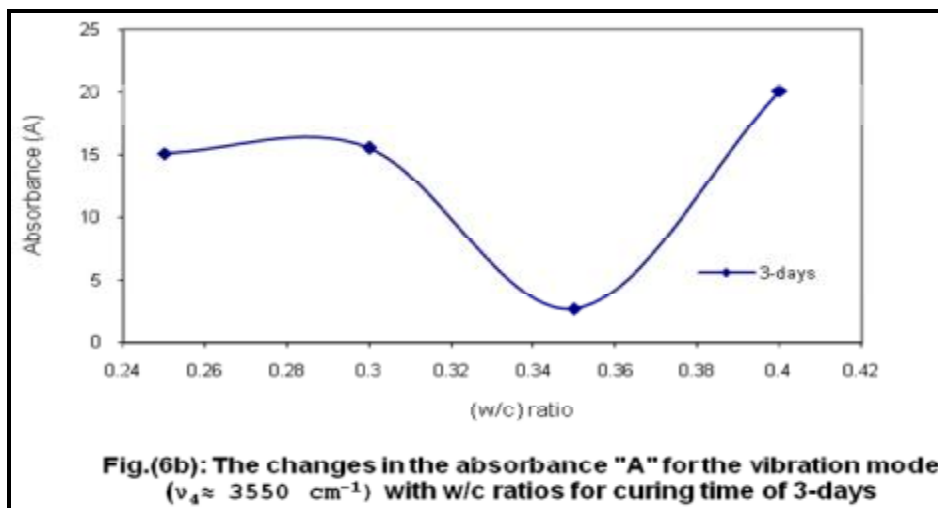
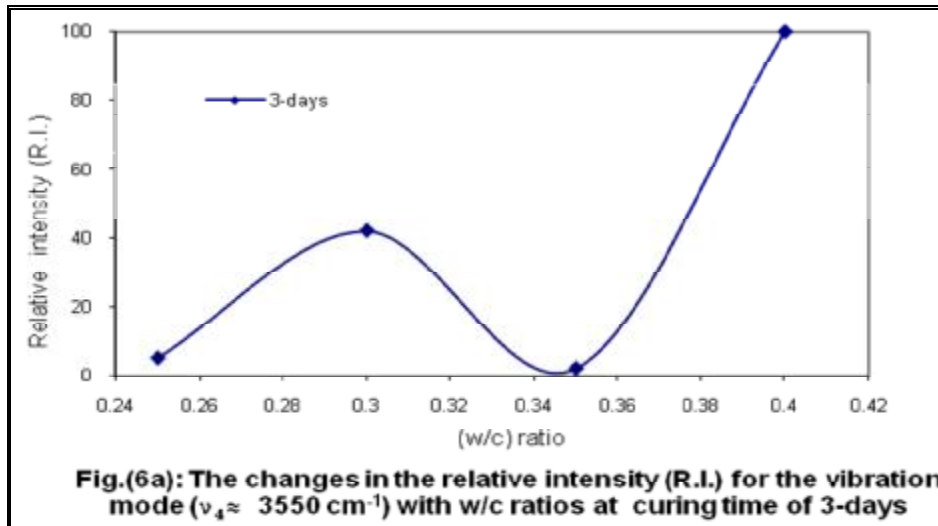
Figure (5a-d), represent the same optical parameters, for the vibration mode ($\nu_3 \approx 1430 \text{ cm}^{-1}$). This mode represents the C=O in the optical matrix for the different samples. The formation and behavior of this mode in all optical parameters (R.I.), (A), (U), and (t) is likely resemble the vibration band mode ($\nu_2 \approx 970 \text{ cm}^{-1}$), whatever the curing time of hydration being 3 or 28 days [14].

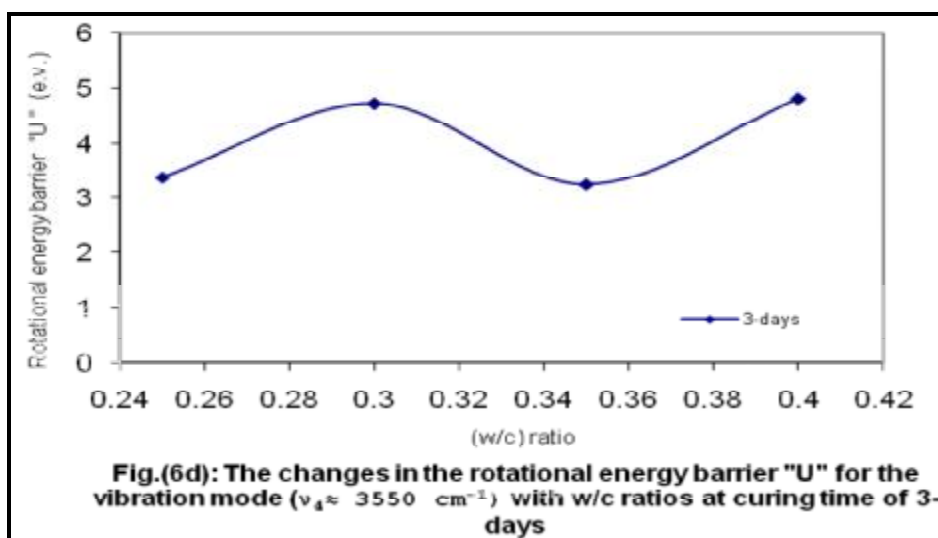
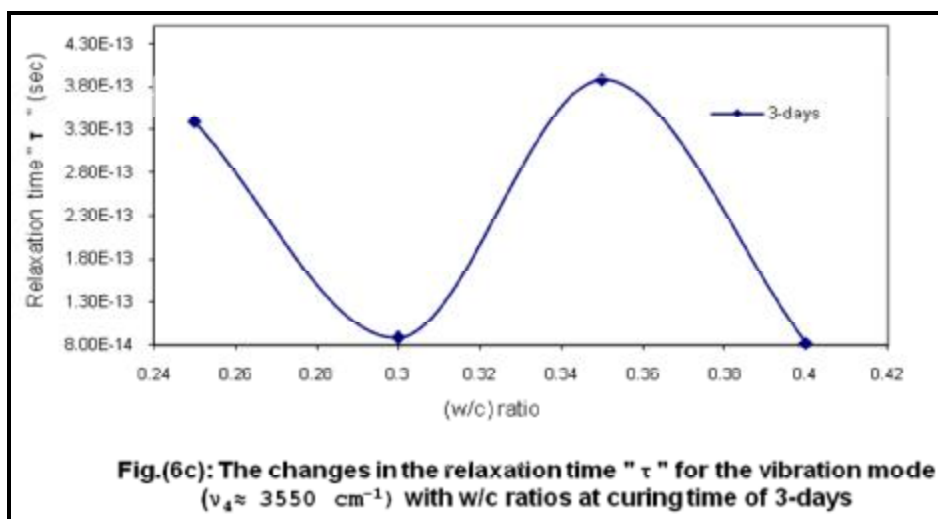




In Figs.(6a-d), the same optical parameters (R.I.), (A), (U), and (t) are studied against the (w/c) ratio and at a curing time of 3 days, for the internal vibration band mode ($\nu_4 \approx 3550 \text{ cm}^{-1}$), which represents the vibration of the OH group in the matrix of the OPC samples. The critical variations in these optical parameters are clearly observed at the (w/c) ratio of 0.30 and 0.35, supporting the obtained results for the vibration modes 460, 970, and 1430 cm^{-1} at the curing time of 3 days. The characteristic peak of ν_4 is often observed as a broad peak which

represents a composite band of several vibrations. For such cement samples, the amount of the retention of water inside the matrix of the sample plays an important role in determining the frequency of the absorption band mode which could be represented as a deformation vibration of the OH bonds in the samples. The variation in this mode, may be related to the variation of the water content and the location of the OH bonds of water in the different samples, i.e., depending on the (w/c) ratio and curing time conditions [2]. The water in the OPC samples has undergone crystallographic changes and phase transformation rates according to the conditions of each sample. The transformation involved is affected by the changes in the primary and secondary bonding.





The curing time and the rate of porosity in each sample are represented as principal parameters for varying and activating such transformation in all variation modes of (n_1, n_2, n_3 , and n_4) [15].

In general, the variation in the (R.I.) for all vibration modes, may be attributed to the differences in the polarizability arising from the production of the free carriers created from the processes of the hydration mechanism. The changes in the shape in the variation modes of (n_1, n_2, n_3 , and n_4) may suggest a probable formation changes in the

crystal structure beginning with the gelatin state of hydration products during the hydration mechanism [16].

Also, the distinct shape of a transmittance band for a particular molecule group band is mainly related to the number of free ions that are involved with various energies during the hydration mechanism of the sample matrix for the OPC system [7,16].

Thus the most intense absorbance (A) change is mainly depending on the largest number of free ions undergoing a particular hydration product formation, and the band envelope as a whole is an indication of the total number of the ion involved [17].

The rotational energy barrier (U), and the relaxation time (t) are inversely proportional to the half band width of the absorption band. The dependence of the rotational energy barrier and the relaxation time on the curing time is clearly observed at the critical (w/c) ratio ≈ 0.30 and 0.35 .

Near these critical conditions of the capillary porosity, the probability of vibration or reorientation of the molecules group considerable change. But at the critical point of variations in all spectroscopic parameters (R.I., A, U, and t), the vibrations or reorientation of the molecular groups change qualitatively, which eventually would lead to a change in the local electric field in the OPC matrix sample. This causes a change in the molecular energy levels and affects the characteristics of the vibrational spectrum of the sample [18].

4. Conclusions:

The main conclusions drawn from this study may be summarized as follows:

1. The change in the rate of hydration can be indicated from the micro-analysis of the FT-IR spectrum by the changes in the accompanied vibration modes, which are formed in the OPC matrix system.
2. All the macroscopic analysis effects of the (w/c) ratio and the curing time on the OPC matrix system, are mainly controlled through the micro-analysis changes in the vibrations modes.
3. Water to cement ratio (i.e., w/c) and the curing time are the most important parameters controlling the variation in the hydration mechanism for the samples.

4. From the micro-analysis of the FT-IR spectrum, it was found that a decrease in frequency band for the stretching vibration of the OH bonds ($n_4 \approx 3550 \text{ cm}^{-1}$) together with an increase in the frequency band of the H₂O groups ($\approx 3600 \text{ cm}^{-1}$), and that indicated the increasing of the rate of hydration especially at a curing time of 28 days.
5. The relative change in relative intensity (R.I.), for the silicate group n_1 , and the carbonyl groups (n_2 , and n_3), also indicated an improvement of the role of the hydration mechanism in the OPC matrix system, due to the of the C-S-H and CH hydrated phase and decreasing the carbonation kinetic in the samples (depending on the (w/c) ratio and the curing time).
6. The critical condition for the changes in all spectroscopic parameters (R.I., A, U, t) for the vibration modes (n_1, n_2, n_3 , and n_4) occurs at (w/c) ≈ 0.30 , and 0.35 (pore structure density effect), whatever the curing time is.
7. At the critical variation in the spectroscopic parameters the vibration or the reorientation of the molecules vibration groups (n_1, n_2, n_3 , and n_4) of the OPC matrix system changes qualitatively (change in the molecular energy levels), and that leads to a change in the characteristics of the vibrational FT-IR spectrum for the OPC matrix system.
8. The changes in the micro-analysis spectrum for the vibration modes (n_1, n_2, n_3 , and n_4) can be reflected to any changes in the physical properties, due to the effect of the (w/c) ratio and the curing time for the hydration mechanism.

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